Spectrochimica Acta, Vol. 43A, No. 4, pp. 475–481, 1987.
Printed in Great Britain.

0584–8539/87 $3.00 + 0.00

The spectra and structure of sulphur-containing organic compounds—V. The vibrational spectra and conformations of p-$RC_6H_4SO_2CH_2X$ sulphones

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(*Received* 1 *May* 1986; *accepted* 24 *July* 1986)

Abstract—The i.r. and Raman spectra of p-$RC_6H_4SO_2CH_2X$ (R = H, CH_3, Cl, Br; X = Cl, Br) sulphone liquid solutions and crystals have been investigated. The existence of a mixture of *trans* and *gauche* conformations in liquid and solution phases has been established. The temperature dependences of the i.r. spectra have been studied and the values of $\Delta H = H(gauche) - H(trans)$ determined. The molecular conformations in the crystal have been determined by the dichroism of polarized i.r. spectral bands. In the case of $CH_3C_6H_4SO_2CH_2Br$ polymorphic crystal modifications, differing in molecular conformations, have been found. An interpretation of the vibrational spectra is given.

INTRODUCTION

$CH_3SO_2CH_2X$ sulphones in liquid and solution phases are in both *trans* and *gauche* conformations [1]. The energy values of the conformations are close and $\Delta H \approx 0$. It is interesting to investigate the effect of the replacement of the CH_3 group by p-RC_6H_4. The conformations of p-$RC_6H_4SO_2CH_2X$ sulphones have been studied only by dipole moment and Kerr's constant methods [2, 3]. It is concluded in Ref. [2] that in a benzene solution the sulphones are in the *gauche* conformation. In the opinion of the authors of Ref. [2] this confirms a new conformation rule, according to which a symmetric arrangement of the polar bonds is disadvantageous. However, it was concluded in [3] that the p-$RC_6H_4SO_2CH_2X$ sulphones in solution are in the form of a mixture of *trans* and *gauche* conformations. Unfortunately, the results of conformational analysis by dipole moment and Kerr's constant methods are materially affected by the choice of parameters. A comparison of Refs [2] and [3] shows that the values of the parameters and their selection are not unambiguous. In this paper an investigation of the vibrational spectra and of the conformations of p-$RC_6H_4SO_2CH_2Cl$ R = H (**I**), CH_3 (**II**), Cl (**III**), Br (**IV**); p-$RC_6H_4SO_2CH_2Br$, R = H (**V**), CH_3 (**VI**), Cl (**VII**), Br (**VIII**) sulphones has been carried out.

EXPERIMENTAL

The i.r. spectra in the 400–4000 cm^{-1} range were measured with a Karl Zeiss UR-20 spectrometer. The Raman spectra were recorded by a DFS-24 He–Ne laser spectrometer. The experimental procedure was similar to that described in [4, 5]. Sulphone **I**–**VIII** synthesis is described in [3].

RESULTS AND DISCUSSION

It can be assumed that, as in the case of haloidmethylsulphone [1], two inequivalent conformations of sulphones **I**–**VIII** are possible with *trans* and *gauche* orientations of the C–X and S–C bonds. The number of conformations in liquid and solution phase was determined by comparing the liquid and crystal spectra. Crystallization of sulphones **I**–**VIII** is accompanied by the disappearance (freezing out) of the following bands in the i.r. spectra and lines in the Raman spectra (Tables 1–4): sulphone **I**, the 517, 585, 708, 723 cm^{-1} bands and the 515 and 711 cm^{-1} lines; sulphone **II**, the 662 cm^{-1} bands and the 213 cm^{-1} line; sulphone **III**, the 463, 546, 568, 1126 cm^{-1} bands and the 223, 287, 463, 544, 666, 702, 798 and 1127 cm^{-1} lines; sulphone **IV**, the 541 cm^{-1} band and the 161, 311 and 538 cm^{-1} lines; sulphone **V**, the 512 and 712 cm^{-1} bands and the 495 cm^{-1} line; sulphone **VII**, the 463, 541 and 564 cm^{-1} bands and the 207, 279, 306, 370, 458, 541 and 564 cm^{-1} lines; sulphone **VIII**, the 541 cm^{-1} band. When the liquid sulphone **VI** film between KBr plates is rapidly or slowly cooled, two crystalline modifications are obtained (crystal I and crystal II), which differ significantly in their i.r. spectra (Table 2, Fig. 1). In the crystal I spectra the 638 and 1199 cm^{-1} bands are frozen out, while in the crystal II spectra this happens to the 626 and 1212 cm^{-1} bands and the 628 cm^{-1} line. In addition, some bands in the crystal I and II spectra differ in relative intensity and position in the spectrum. For example, the 464 and 516 cm^{-1} bands are observed in the i.r. spectrum of liquid sulphone **VI**, 461 and 520 cm^{-1} bands correspond to them in the crystal I spectrum, and the 478 and 507 cm^{-1} bands in the crystal II spectrum (Table 2).

These experimental data on the vibrational spectra of sulphones **I**–**VIII** may be explained only by the presence of a mixture of *trans* and *gauche* conformations in liquid sulphones. Only one of them remains

See Part IV, A. B. REMIZOV, F. S. BILALOV and I. S. POMINOV, *Spectrochim Acta*, in press.

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